

D E C L A R A T I O N

In the matter of U.S. Patent  
Appln. Ser. No. 09/374,344  
in the name of TOTO LTD.

I, KONNO Akio, of Kyowa Patent and Law Office, 2-3,  
Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare  
and say:

that I am thoroughly conversant with both the Japanese  
and English languages; and,

that the attached document represents a true English  
translation of Japanese Patent Application No. 7-182019  
filed on June 14, 1995.

I further declare that all statements made herein of  
my own knowledge are true and that all statements made on  
information and belief are believed to be true; and further  
that these statements were made with the knowledge that  
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18 of the United States Code, and that such willful false  
statements may jeopardize the validity of the application  
or any patent issued thereon.

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APPLICATION TO FORM THEREOF

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List of Documents filed:

Specification	1
Drawing	1
Abstract	1

SPECIFICATION

1. TITLE OF THE INVENTION

A STAIN-RESISTANT MEMBER AND APPLICATION TO FORM THEREOF

2. CLAIMS

1. A stain-resistant member having an exposed surface hydrophilic and a means for maintaining thereof.
2. A stain-resistant member wherein a surface layer having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface.
3. A stain-resistant member according to claims 1 - 2, wherein said means for maintaining an exposed surface hydrophilic is a photocatalyst.
4. A stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance.
5. A stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface.
6. A stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface.

7. A stain-resistance member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface, and an exposed surface is comprised of a hydrophilic substance non-photocatalytic.

8. A stain-resistant member according to claims 5 - 7, wherein an intermediate layer is interleaved between a substrate and a surface layer.

9. A stain-resistant member according to claim 4, wherein said film comprised of a hydrophilic substance is a photo-resistant resin subjected to a hydrophilization process.

10. A stain-resistant member according to claims 6 - 8, wherein said hydrophilic substance non-photocatalytic is a photo-resistant resin subjected to a hydrophilization process.

11. A stain-resistant member according to claims 6 - 8, wherein said hydrophilic substance non-photocatalytic is an inorganic amorphous substance.

12. A stain-resistant member according to claims 5 - 8, wherein said hydrophilic substance is a particle that improves filling of an exposed surface.

13. A stain-resistant member according to claims 5 - 8, wherein said hydrophilic substance is a sintering assistant

of a photocatalytic particle hydrophilic.

14. A stain-resistant member according to claims 9 - 10, wherein said photo-resistant resin subjected to a hydrophilization process is a resin having a Si-O or Si-N bond in a skeleton part.

15. A stain-resistant member according to claims 9 - 10 or 14, wherein said hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a resin wherein at least a skeleton part is comprised of a photo-resistant component.

16. A stain-resistant member having a surface layer comprised of a resin comprised of a photo-resistant component and a photocatalyst, and having a hydrophilic surface simply by light irradiation.

17. A stain-resistant member wherein a photocatalyst is added to a film comprised of a resin comprised of a photo-resistant component, and having a hydrophilic surface simply by light irradiation.

18. A stain-resistant member having a surface layer comprised of a resin having a Si-O or Si-N bond in a skeleton part and a photocatalyst.

19. A stain-resistant member wherein a photocatalyst is added to a film comprised of a resin having a Si-O or Si-N bond in a skeleton part.

20. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, and 18, wherein an electron uptake metal is included in said surface layer.
21. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, and 18, wherein an antibacterial metal is included in said surface layer.
22. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, and 18, wherein silver is included in said surface layer.
23. A stain-resistant member according to claims 4, 9 or 17, and 19, wherein an electron uptake metal is included in said film.
24. A stain-resistant member according to claims 4, 9 or 17, and 19, wherein an antibacterial metal is included in said film.
25. A stain-resistant member according to claims 4, 9 or 17, and 19, wherein silver is included in said film.
26. A stain-resistant member according to claims 8, 10 - 13, and 20 - 22, wherein said intermediate layer is comprised of a thermoplastic binder.
27. A stain-resistant member according to claims 8, 10 - 13, and 20 - 22, wherein said intermediate layer is comprised of glaze.

28. A stain-resistant member according to claims 14 - 16 and 18, wherein said intermediate layer is comprised of a base coat layer comprised of a resin.
29. A stain-resistant member according to claims 8, 10 - 16, 18, and 20 - 22, wherein said substrate is comprised of a substance including an alkali modification component, and said intermediate layer is a layer that prevents diffusion of an alkali modification component.
30. A stain-resistant member according to claims 5, 6, 8, 12, 13, 20 - 22, and 24 - 26, wherein said intermediate layer is formed by a substance with a melting point higher than that of a substrate.
31. A stain-resistant member according to claims 29 and 30, wherein said layer that prevents diffusion of an alkali modification component is a a high purity silica layer.
32. A stain-resistant member according to claims 29 and 30, wherein said layer that prevents diffusion of an alkali modification component is a layer including an electron uptake metal.
33. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, 18, 20 - 22, and 26 - 32, wherein a photocatalyst with a thickness exceeding 0.3  $\mu$ m exists over said surface layer.
34. A stain-resistant member according to claims 5 - 8,



10 - 16, 18, 20 - 22, and 26 - 33, wherein the stain-resistant member according to claims 4, 9, 17, 19, and 23 - 25 is stuck or bonded on a substrate surface.

35. An application including a photocatalyst and a photo-resistant resin to form a stain-resistant member according to claims 9, 10, 14 - 25, 28, and 34.

36. A stain-resistant member or an application wherein the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 95% or less, in a stain-resistant member according to claims 9, 10, 14 - 25, 28 and 34, or an application according to claim 35.

37. A stain-resistant member or an application wherein the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 60% or less, in a stain-resistant member according to claims 9, 10, 14 - 25, 28 and 34, or an application according to claim 35.

38. A stain-resistant member providing a UV irradiating means on at least a part of the rim of the stain-resistant member according to claims 1 - 34, or 36 and 37.

39. A stain-resistant member according to claim 38, wherein a UV reflecting means is provided around a UV irradiating means.

40. A stain-resistant member providing a UV irradiating means on the back of the stain-resistant member according to claims 1 - 34, or 36 and 37.

41. A stain-resistant member providing a UV irradiating means on the intermediate layer of the stain-resistant member according to claims 1 - 34, or 36 and 37.

42. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 18, 20 - 22, 26 - 34, and 35 - 41, wherein said substrate is an external wall building material.

43. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 18, 20 - 22, 26 - 34, and 36 - 41, wherein said substrate is a substrate used in a water environment such as a bathtub, washbowl, toilet, and interior tile.

44. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 18, 20 - 22, 26 - 34, and 36 - 41, wherein said substrate is a floor tile.

45. A stain-resistant member according to claims 1 - 34 and 36 - 44, wherein a contact angle with water on a member surface is 30° or less.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a member having stain-resistance, in a member used in a water environment such as

a bathtub, bathroom inner wall material, bathroom floor material, soap case, bathroom article like a mirror, washbowl, sink, toilet, washing machine, a raincoat and paper diaper; a member used outdoors exposed by rain such as an exterior building material; or a member used under an environment cleaned with water such as a tunnel inner wall material.

[0002]

[Prior Art]

Conventionally, inorganic, plastic, metal, or fiber material, or composite thereof is used for the member used in a water environment or the member used outdoors.

To provide these materials with stain resistance, there are methods of forming a water-repellent resin film on a member surface, and of forming a hydrophilic resin film on a member surface.

[0003]

However, there is a problem that a method of forming a water-repellent resin film like polytetrafluoroethylene on a member surface, leaves fur after water is dried on the member, so that the stain is noticeable.

To solve the problem, recently it has been suggested that hydrophilicity is provided with on the surface of a member used in a water environment or a member used outdoors ("Highpolymer", vol. 44, page 307 (1995)).

[0004]

In other words, a hydrophilic member surface leaves no fur because the surface conforms to water and not to organic stains such oil, even when dirty water including the stains is flown.

[0005]

Conventionally, two methods have been known to render a member surface hydrophilic.

One is to form a member surface with an inorganic amorphous material. The favorable examples are an enamel bathtub, glazed tile, sanitary ware, glass, and mirror.

The other is to form a member surface with a hydrophilic resin such as acrylic, acrylic-styrene ("Highpolymer", vol. 44, page 307 (1995)), polyamide, and polyvinylidene fluoride.

[0006]

[Problems to be Solved by the Invention]

However, both of the conventional methods of rendering a member surface hydrophilic cannot maintain hydrophilicity over a long period.

For example, glass shows a favorable result of a contact angle with water of about 5 - 20° at production; but the glass surface absorbs gradually a polar component such as lower carboxylic acid, being rendered hydrophobic ("Design of Glass Surface", Kindai Henshu-sha (1983)). It is understood that a method of forming with a hydrophilic resin also would produce the same phenomenon. It is an object of the present invention to offer a member that prevents adhesion of organic stains like oil for a long period.

[0007]

[Means to Solve the Problems]

To solve the above problems, the present invention offers a stain-resistant member having an exposed surface hydrophilic and a means for maintaining thereof.

[0008]

In the preferable embodiment of the present invention, a surface layer having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface.

[0009]

In the preferable embodiment of the present invention, the means for maintaining an exposed surface hydrophilic is a photocatalyst.

[0010]

In the preferable embodiment of the present invention, a photocatalyst is added to a film comprised of a hydrophilic substance.

[0011]

In the preferable embodiment of the present invention, a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface.

[0012]

In the preferable embodiment of the present invention, a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface.

[0013]

In the preferable embodiment of the present invention, a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface, and an exposed surface is comprised of a hydrophilic substance non-photocatalytic.

[0014]

In the preferable embodiment of the present invention,

an intermediate layer is interleaved between a substrate and a surface layer.

[0015]

In the preferable embodiment of the present invention, the film comprised of a hydrophilic substance is a photo-resistant resin subjected to a hydrophilization process.

[0016]

In the preferable embodiment of the present invention, the hydrophilic substance non-photocatalytic is a photo-resistant resin subjected to a hydrophilization process.

[0017]

In the preferable embodiment of the present invention, the hydrophilic substance non-photocatalytic is an inorganic amorphous substance.

[0018]

In the preferable embodiment of the present invention, the hydrophilic substance is a particle that improves filling of an exposed surface.

[0019]

In the preferable embodiment of the present invention, the hydrophilic substance is a sintering assistant of a photocatalytic particle hydrophilic.

[0020]

In the preferable embodiment of the present invention, the photo-resistant resin subjected to a hydrophilization process is a resin having a Si-O or Si-N bond in a skeleton part.

[0021]

In the preferable embodiment of the present invention, the hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a resin wherein at least a skeleton part is comprised of a photo-resistant component.

[0022]

In the preferable embodiment of the present invention, a surface layer comprised of a resin comprised of a photo-resistant component and a photocatalyst is provided, and a hydrophilic surface is provided simply by light irradiation.

[0023]

In the preferable embodiment of the present invention, a photocatalyst is added to a film comprised of a resin comprised of a photo-resistant component, and a hydrophilic surface is provided simply by light irradiation.

[0024]

In the preferable embodiment of the present invention, a surface layer comprised of a resin having a Si-O or Si-N bond in a skeleton part and a photocatalyst is provided.

[0025]

In the preferable embodiment of the present invention, a photocatalyst is added to a film comprised of a resin having a Si-O or Si-N bond in a skeleton part.

[0026]

In the preferable embodiment of the present invention, an electron uptake metal is included in the surface layer.

[0027]

In the preferable embodiment of the present invention,

an antibacterial metal is included in the surface layer.

[0028]

In the preferable embodiment of the present invention, silver is included in the surface layer.

[0029]

In the preferable embodiment of the present invention, an electron uptake metal is included in the film.

[0030]

In the preferable embodiment of the present invention, an antibacterial metal is included in the film.

[0031]

In the preferable embodiment of the present invention, silver is included in the film.

[0032]

In the preferable embodiment of the present invention, the intermediate layer is comprised of a thermoplastic binder.

[0033]

In the preferable embodiment of the present invention, the intermediate layer is comprised of glaze.

[0034]

In the preferable embodiment of the present invention, the intermediate layer is comprised of a base coat layer comprised of a resin.

[0035]

In the preferable embodiment of the present invention, the substrate is comprised of a substance including an alkali modification component, and the intermediate layer is a layer that prevents diffusion of an alkali modification component.



[0036]

In the preferable embodiment of the present invention, the intermediate layer is formed by a substance with a melting point higher than that of a substrate.

[0037]

In the preferable embodiment of the present invention, the layer that prevents diffusion of an alkali modification component is a high purity silica layer.

[0038]

In the preferable embodiment of the present invention, the layer that prevents diffusion of an alkali modification component is a layer including an electron uptake metal.

[0039]

In the preferable embodiment of the present invention, a photocatalyst with a thickness exceeding  $0.3 \mu\text{m}$  exists over the surface layer.

[0040]

In the preferable embodiment of the present invention, the film-like stain-resistant member is stuck or bonded on a substrate surface.

[0041]

In the preferable embodiment of the present invention, an application to form a stain-resistant film having said surface layer comprised of a photocatalyst and a photo-resistant resin, is provided.

[0042]

In the preferable embodiment of the present invention, the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 95% or less.

[0043]

In the preferable embodiment of the present invention, the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 60% or less.

[0044]

In the preferable embodiment of the present invention, a UV irradiating means is provided on at least a part of the rim of the stain-resistant member.

[0045]

In the preferable embodiment of the present invention, a UV reflecting means is provided around a UV irradiating means.

[0046]

In the preferable embodiment of the present invention, a UV irradiating means is provided on the back of the stain-resistant member.

[0047]

In the preferable embodiment of the present invention, a UV irradiating means is provided on the intermediate layer of the stain-resistant member.

[0048]

In the preferable embodiment of the present invention, the substrate is an external wall building material.

[0049]

In the preferable embodiment of the present invention, the substrate is a substrate used in a water environment such as a bathtub, washbowl, toilet, and interior tile.

[0050]

In the preferable embodiment of the present invention,

the substrate is a floor tile.

[0051]

In the preferable embodiment of the present invention, a contact angle with water on a member surface is 30° or less.

[0052]

[Effect of the Invention]

An exposed surface hydrophilic and a means for maintaining thereof are provided, to make a member that prevents adhesion of organic stains like oil for a long period.

[0053]

A layer surface having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface, so that the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0054]

A means for maintaining a hydrophilic surface is a photocatalyst, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilic surface can be maintained for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0055]

A photocatalyst is added to a film comprised of a hydrophilic substance, so that only irradiating a UV light

such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity of the film surface comprised of a hydrophilic substance can be maintained for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0056]

A surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0057]

A surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0058]

A surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic

is formed on a substrate surface, and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0059]

A intermediate layer is interleaved between a substrate and a surface layer, so that a variety of functions can be added to the intermediate layer.

[0060]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance is a photo-resistant resin rendered hydrophilic, so that the photocatalyst and resin are mixed in a liquid to be applied or molded on the substrate, that is then simply treated at a room temperature to low temperatures of about 300°C to preferably make the above stain-resistant member.

[0061]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance non-photocatalytic is an inorganic amorphous substance, so that a function to maintain the hard stain resistance on the member surface for a long period can preferably be added.

[0062]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface; a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance non-photocatalytic is a particle that improves filling of the exposed surface, so that a surface layer having a function to maintain the stain resistance with more

than constant film strength even at low temperatures wherein the photocatalyst occurs no neck growth, can preferably be added.

[0063]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface; a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance non-photocatalytic is a sintering assistant of a photocatalytic particle hydrophilic to realize sintering of the surface layer at lower temperatures, so that a surface layer having a function to maintain the stain resistance with more than constant film strength by controlling lowered activity due to particle growth of the photocatalytic particle, can preferably be added.

[0064]

A photo-resistant resin rendered hydrophilic is a resin having a Si-O or Si-N bond in a skeleton part, so that preferably the Si-O or Si-N bond has hydrophilicity, and a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin having these bonds in a skeleton part have the most excellent photo resistance in the resins.

[0065]

A hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a resin wherein at least a skeleton part is comprised of a photo-resistant component, so that a hydrophilic surface with a sufficient film strength can easily be formed, unlike the case where a hydrophilic resin such as polyamide and polyvinylidene fluoride is added directly to a member surface.

[0066]

A member having a surface layer comprised of a resin comprised of a photo-resistant component and a photocatalyst, and having a hydrophilic surface only by light irradiation is formed, so that in the case where a member such as an external wall material used in a sunray-irradiated environment or housing facility equipment used in an environment subjected to indoor illumination, a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance. In addition, a component decomposed by UV irradiation should exist until a surface layer is formed, giving flexibility and promoting cross-link.

[0067]

A member wherein a photocatalyst is added to a film comprised of a resin comprised of a photo-resistant component, and having a hydrophilic surface only by light irradiation is formed, so that in the case where a member such as an external wall material used in a sunray-irradiated environment or housing facility equipment used in



an environment subjected to indoor illumination, a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance. In addition, a component decomposed by UV irradiation should exist until a surface layer is formed, giving flexibility and promoting cross-link.

[0068]

A member having a surface layer comprised of a resin having a Si-O or Si-N bond in a skeleton part and a photocatalyst is formed, so that in the case where a member such as an external wall material used in a sunray-irradiated environment or housing facility equipment used in an environment subjected to indoor illumination, a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance.

[0069]

A member wherein a photocatalyst is added to a film comprised of a resin having a Si-O or Si-N bond in a skeleton part is bonded or stuck on an external wall material used in a sunray-irradiated environment or housing facility equipment used in an environment subjected to indoor illumination, so that a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance.

[0070]

An electron uptake metal is included in a surface

layer, so that in addition to the above stain-resistant effect, especially a deodorizing function based on a photocatalytic function improves preferably to a large extent.

[0071 ]

An antibacterial metal is included in a surface layer, so that in addition to the above stain-resistant effect, the synergistic effect of a photocatalytic function and the antibacterial metal delivers sufficient antibacterial power on a member surface. In addition, in the case where a member is used in a water or rain-exposed environment, addition of the antibacterial metal releases the antibacterial metal in the water, rendering preferably water itself antibacterial.

[0072]

Silver is included in a surface layer, so that the above antibacterial property can preferably be delivered without lowering a hydrophilicity maintaining function by a photocatalyst.

[0073]

An electron uptake metal is included in a film, so that in addition to the above stain-resistant effect, especially a deodorizing function based on a photocatalytic function improves preferably to a large extent.

[0074]

An antibacterial metal is included in a film, so that in addition to the above stain-resistant effect, the synergistic effect of a photocatalytic function and the antibacterial metal delivers sufficient antibacterial power on a member surface. In addition, in the case where a member

is used in a water or rain-exposed environment, addition of the antibacterial metal releases the antibacterial metal in the water, rendering preferably water itself antibacterial.

[0075]

Silver is included in a film, so that the above antibacterial property can preferably be delivered without lowering a hydrophilicity maintaining function by a photocatalyst.

[0076]

An intermediate layer is comprised of a thermoplastic binder, so that the thermoplastic binder is applied on a substrate, followed by a photocatalyst, and then the substrate is simply heat-treated at temperatures lower than the heat-resistant temperature of the substrate and higher than the softening temperature of the thermoplastic binder, a surface layer having a function to maintain the stain resistance with more than constant film strength, can preferably be added.

[0077]

An intermediate layer is comprised of glaze, so that the texture, decorative property, and excellent chemical stability of the surface can be maintained.

[0078]

An intermediate layer is comprised of a base coat layer comprised of a resin, so that the following 5 effects are provided. First, a substrate and a surface layer can be combined more strongly to improve peel resistance. A film made only of a resin has a film strength higher than that of a film made of a mixture of a resin and a photocatalyst, and has excellent adhesion.

[0079]

Second, improvement of the peel resistance of a film can increase the ratio of the photocatalyst in a surface layer at the same film strength, improving an effect of maintaining hydrophilicity higher.

[0080]

Third, when the effect of maintaining hydrophilicity by a photocatalyst is constant, a photocatalyst can be concentrated on a surface layer, providing a thinner surface layer.

[0081]

Fourth, the resin on a surface layer should have photo-resistance in a highpolymer skeleton part and be a resin to be rendered hydrophilic (resin comprised mainly of a Si-O or Si-N bond), but a resin forming a base coat layer can be selected freely. Therefore, forming a base coat layer with more inexpensive resin, can reduce production cost.

Also, when the thermal expansion coefficient difference between a substrate and a surface layer is different significantly, an elastic resin or a resin having an intermediate thermal expansion coefficient is used to form a base coat layer, any crack at heat treatment can be prevented.

[0082]

Fifth, when a substrate is uneven largely, the surface of it can be smoothed with a base coat layer, providing the following effects.

An outermost surface layer can easily be smoothed. The smooth outermost surface layer allows a light to be

efficiently irradiated on a photocatalyst, delivering an effect of maintaining hydrophilicity more effectively. Also, a photocatalyst exists over the whole film almost uniformly, so that the effect of maintaining hydrophilicity can be delivered uniformly over the whole surface of the substrate.

[0083]

A substrate is comprised of a substance including an alkali modification component and an intermediate layer is a layer that prevents diffusion of an alkali modification component, so that surface diffusion of the alkali modification component in the substrate can be prevented during producing or using a member, and lowering of a hydrophilicity maintaining function due to adhesion of an alkali metal or alkaline earth metal to a photocatalytic active point can be controlled.

[0084]

An intermediate layer is made of a substance having a melting point higher than that of a substrate, so that in the case where a substrate is made of a low melting point material like soda glass, a surface layer is resistant to be imbedded in a substrate during producing a member, delivering a hydrophilicity maintaining function more efficiently.

[0085]

A layer that prevents diffusion of an alkali modification component is a high purity silica layer, so that, since the self-diffusing coefficient in the high purity silica layer at low temperatures of the alkali modification component is extremely low, surface diffusion

of the alkali modification component in the substrate can be prevented during producing or using a member, and lowering of a hydrophilicity maintaining function due to adhesion of an alkali metal or alkaline earth metal to a photocatalytic active point can be controlled.

[0086]

A layer that prevents diffusion of an alkali modification component is a layer including an electron uptake metal, so that surface diffusion of the alkali modification component in the substrate can be prevented during producing or using a member, and lowering of a hydrophilicity maintaining function due to adhesion of an alkali metal or alkaline earth metal to a photocatalytic active point can be controlled, improving a photocatalytic function. Therefore, a deodorizing function based on a photocatalyst is improved.

[0087]

A photocatalyst with a thickness exceeding  $0.3 \mu\text{m}$  exists over the whole surface layer, so that decomposition for an adhered polar organic molecule can preferably be performed immediately.

[0088]

The above film-like stain-resistant member is stuck or bonded on a substrate surface, so that the hydrophilicity can easily be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0089]

A stain-resistant member having a surface layer comprised of the above photocatalyst and photo-resistant

resin can be made even at low temperatures of 150°C or less, so that application including the photocatalyst and photo-resistant resin, is applied on a substrate like existing housing facility equipment and external wall material, if necessary, with a curing agent or a base coat layer forming agent, and heat-treated thereof with a burner to make a member.

[0090]

In a stain-resistant member having a surface layer comprised of the above photocatalyst and photo-resistant resin, the ratio by weight of said photocatalyst versus the sum of the photocatalyst and photo-resistant resin is 5% or more and 95% or less, so that the member has a hydrophilicity maintaining effect and favorable wear resistance.

This effect is decisively different from conventionally known a deodorizing effect and effect due to direct oxidative-decomposing action of the photocatalyst such as stain resistance of nicotine. In other words, the effect due to direct oxidative-decomposing action of the photocatalyst like a deodorizing effect becomes weak, when the photocatalyst is covered by a binder or resin, or the mixed ratio of the photocatalyst is low. On the contrary, the main part in stain resistance by the hydrophilicity maintaining effect is a hydrophilic surface; to maintain the function, the photocatalyst should oxidatively decomposes only a further adhered polar molecule. Therefore, the effect can be obtained even when the photocatalyst is covered by a binder and resin, and has a small amount of about 5% by weight.

[0091]

In a stain-resistant member having a surface layer comprised of the above photocatalyst and photo-resistant resin, the ratio by weight of said photocatalyst versus the sum of the photocatalyst and photo-resistant resin is 5% or more and 60% or less, so that the member has a hydrophilicity maintaining effect, favorable wear resistance and sufficient hardness.

[0092]

A UV irradiating means is provided on at least a part of the rim of a stain-resistant member, so that a light source is placed thereon more closely compared with an indoor illumination and sunray, irradiating a UV with a higher intensity on the member surface. Therefore, the hydrophilicity maintaining effect can be realized for a shorter time.

[0093]

A UV reflecting means is provided around the UV irradiating means, so that the UV intensity irradiated on a member surface can be improved, realizing the hydrophilicity maintaining effect can be realized for a shorter time.

[0094]

A UV irradiating means is provided on the back of a stain-resistant member, so that a light source is placed thereon more closely compared with an indoor illumination and sunray, irradiating a UV with a higher intensity on the member surface. Therefore, the hydrophilicity maintaining effect can be realized for a shorter time.

Also, the UV irradiating means is a flat light source, so that the flat light source is simply fixed on the back of



the member by sticking, bonding and baking, e.g. at the end of the step, providing the UV irradiating means easily.

[0095]

A UV irradiating means is provided on the intermediate layer of a stain-resistant member, so that a light source is placed thereon more closely compared with an indoor illumination and sunray, irradiating a UV with a higher intensity on the member surface. Therefore, the hydrophilicity maintaining effect can be realized for a shorter time.

Also, the UV irradiating means is a flat light source, so that the flat light source is simply fixed by sticking, bonding and baking, e.g. in the middle of the step, providing the UV irradiating means easily.

[0096]

The above stain-resistant member is applied to an external wall material, so that the hydrophilicity of the surface thereof is maintained to make an external wall material wherein stains can easily be washed off simply by throwing rain or water.

[0097]

The above stain-resistant member is applied to a member used in a water environment such as a bathtub, washbowl, toilet, and interior tile, so that the hydrophilicity of the surface thereof is maintained to make a member that is resistant to stains due to continuous use.

[0098]

The above stain-resistant member is applied to a floor tile, so that the hydrophilicity of the surface thereof is maintained to make a member that is resistant to stains due

to continuous use and to be hard to slide.

[0099]

Rendering a member surface hydrophilic is made to a degree that the contact angle with water is  $30^\circ$  or less, so that the member is resistant to heavy stains.

[0100]

[Embodiment]

The concrete construction of the present invention is explained based on embodiments. An exposed surface hydrophilic is an exposed surface that shows the hydrophilicity to a degree that stains are resistant, and has a contact angle with water of less than  $30^\circ$ , more preferably less than  $10^\circ$ . This is explained concretely below.

Fig. 1 is a diagram using various resins to check the relation between a contact angle with water and stain adhesion.

The contact angle with water was checked with a contact angle measuring instrument; in the stain adhesion, as shown in Fig. 2, a sample was immersed in an artificial bathtub water (warm water mixed with human being's dirt, lard, and soap) for 3 hours to find specific glossiness around a level surface before and after immersion for an evaluating index. The specific glossiness is glossiness after immersion when an initial glossiness before immersion is 1.

According to Fig. 1, the specific glossiness was lowest around a contact angle with water of  $70^\circ$  to be easy to stain adhesion. The specific glossiness is better for the low angle than for the high angle, and showed almost no change for the angle of less than  $30^\circ$ .

It is evident from the above, that a contact angle with water is less than  $30^\circ$ , showing hydrophilicity to a degree that a stain is resistant.

[0101]

The hydrophilic substance refers to a substance that has an extremely low contact angle with water when no component including both of a hydrophilic group like lower carboxylic acid and a hydrophobic group adheres to a surface. Concretely, examples preferably usable include an inorganic crystalline oxide material such as crystalline alumina, zirconia, titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, dibismuth trioxide and tin oxide; an inorganic amorphous material such as glaze and glass; a resin comprised of a Si-O or Si-N bond of a silicon resin and silazane resin; and a resin having a metal-oxygen bond like a Ti-O bond.

[0102]

The means for maintaining an exposed surface hydrophilic refers to a means that can prevent the exposed surface from being rendered hydrophobic, or can recover the hydrophilicity of the exposed surface rendered hydrophobic; for example, a photocatalyst can preferably be used.

[0103]

For example, the following 2 embodiments can be considered for a stain-resistant member having an exposed surface hydrophilic and a means for maintaining thereof.

One is a film-like stain-resistant member comprised of an exposed surface hydrophilic and a means for maintaining thereof.

In this case, when the means for maintaining an exposed

surface hydrophilic is a photocatalyst, the embodiment like Fig. 3 can be considered.

Fig. 3 shows a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance.

[0104]

The other is a stain-resistant member wherein a surface layer having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface.

In this case, when the means for maintaining an exposed surface hydrophilic is a photocatalyst, for example, Figs. 4 - 6 can be considered.

In Fig. 4, a surface layer is made of a hydrophilic photocatalyst; in Fig. 5, a surface layer is made of a hydrophilic photocatalyst and a hydrophilic substance; and in Fig. 6, a surface layer is made of a photocatalyst and a hydrophilic substance, and an exposed surface is made only of a hydrophilic substance.

[0105]

The photocatalyst refers to a substance that can generate an electron and a hole by light irradiation with less than a constant wavelength, and as a result, produce active oxygen. Examples having hydrophilicity in these substances include titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, dibismuth trioxide and tin oxide.

The irradiated light sources with less than a constant wavelength, are e.g. a sunray, fluorescent lamp, mercury lamp, incandescent lamp, xenon lamp, BLB lamp, metal halide lamp, iron illuminant lamp and germicidal lamp.

[0106]

Any material for the substrate may basically be used; for example, ceramic, pottery material, metal, glass, plastic, decorative plywood, calcium silicate, mortar, steel plate, paper or composite thereof.

[0107]

The particle that improves filling of an exposed surface refers to a particle that, in generation of a gap like an interstice on a substrate surface, has a particle diameter smaller than the gap and bridges the gap.

The generation of a gap like an interstice on a substrate surface includes both of forming and after calcining. Example of the generation of a gap like an interstice on a substrate surface at forming, is e.g. application of a photocatalytic sol or a photocatalytic particle to a substrate.

A mixed particle for particle-size mixing with a photocatalytic sol or a photocatalytic particle, and a particle that bridges a gap by after-application to a substrate, are applied to the particle that improves filling in this case. Example of the generation of a gap like an interstice on a substrate surface after calcining, is e.g. calcining without rendering the surface dense after a photocatalytic sol or a photocatalytic particle is applied to the substrate.

A mixed particle for particle-size mixing with a photocatalytic sol or a photocatalytic particle, and a particle that bridges a gap by after-application to a substrate before or after calcining, are applied to the particle that improves filling in this case.

[0108]

The sintering assistant refers to an assistant added to give more than constant film strength to a surface layer at low temperatures. For example, tin oxide can favorably be used for a titanium oxide sintering assistant. Preferably, a sintering assistant wherein its sintering mechanism depends on steam-condensation should be better; because the assistant is sintered without condensation, being resistant to cracks at production.

[0109]

The photo-resistant resin refers to a good photo-resistant resin, such as a silicon resin, siloxane resin, fluoro resin, and polysilazane resin, that has a photo-resistant bond such as a Si-O, Si-N, C-F, and Si-F bond.

[0110]

The resin comprised of at least a photo-resistant component in a skeleton part, refers to a resin wherein a main bond that is not an end functional group is comprised of a photo-resistant bond such as a Si-O, Si-N, C-F, and Si-F bond.

[0111]

The hydrophilization process refers to a process oxidizing or decomposing a hydrophobic functional group like an alkyl group to change into a hydrophilic functional group such as a hydroxide or carboxyl group. To perform this, there are, e.g. methods of UV irradiation, contacting of an oxidizing agent such as hydrogen peroxide and ozone, and heating.

[0112]

The electron uptake metal refers to a metal such as Pt,

Pd, Ag, Cu, Au, Ni, Co and Fe, that has a low ionization tendency and is easily self-reduced.

[0113]

The antibacterial metal refers to a metal or ion showing an antibacterial action, or a retainer thereof. For example, a metal such as silver, copper and zinc, or ion thereof is retained to zeolite, apatite, calcium phosphate, zirconium phosphate, aluminum phosphate, titania, and zinc oxide.

[0114]

The thermoplastic binder refers to a binder softened by heating. The example is an organic binder such as glaze, glass and polyvinyl alcohol.

[0115]

The base coat layer refers to a resin layer interleaved between a substrate and a surface layer.

[0116]

The substance including an alkali modification component refers to a substance including alkaline metal, alkaline earth metal or ion thereof. The examples are ceramic including alkaline metal, alkaline earth metal or ion thereof in soda glass, soda-lime glass, sheet glass, sintering agent and impurity; and plastic, fiber and metal including alkaline metal, alkaline earth metal or ion thereof in impurity.

[0117]

The layer that prevents diffusion of an alkali modification component refers to a layer that makes the alkaline modification component in the above substrate hard to reach a surface layer; basically any dense layer not

including an alkaline modification component may be used. The examples are a high purity silica layer, resin layer not including an alkaline modification component, metal layer, ceramic layer or composite thereof.

[0118]

The UV light refers to a light such as a sunray, indoor illumination lamp and illumination belonging to a member, that includes a UV. The kind of the light source should include a UV. The examples are a fluorescent lamp, incandescent lamp, UV lamp, xenon lamp, mercury lamp, BLB lamp, and metal halide lamp.

The UV irradiating means refers to an illumination belonging to a member. It is provided so that a light source is placed at a position closer to a member surface, irradiating a UV with a higher intensity thereon.

[0119]

A method of making a stain-resistant member shown in Figs. 3 - 6, is explained. For an antifogging transparent member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermosetting resin (siloxane resin); and the photocatalyst is anatase-form titanium oxide.

The method is comprised of the steps of: adding a siloxane resin to a anatase-form titanium oxide sol to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, putting the liquid into a mold for heat-curing and mold-release to obtain an intermediate member,



and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0120]

[Formula 1]

[0121]

Preferably, the anatase-form titanium oxide sol is sufficiently dispersed in a suspension. For that reason, the anatase-form titanium oxide that has an isoelectric point of pH 6.5, is dispersed under acidic or alkaline conditions. Any dispersing solvent may basically be used, but water and alcohol are safe and easy to use.

[0122]

After the siloxane resin is added to the anatase-form titanium oxide sol, the diluent is added to lower the viscosity of the liquid and make flowing thereof into the mold easy. Therefore, any kind of diluent to reach this aim may be used, but water and alcohol are safe and easy to use. Also, if the viscosity of the liquid is sufficiently low without adding a diluent, the diluent is not necessarily required.

[0123]

The siloxane resin is added to the anatase-form titanium oxide sol, the diluent is added thereto, followed by the curing agent, to make the liquid, so that a liquid to be applied to a substrate can be generated without agglomerating a suspension.

[0124]

For a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermosetting resin (siloxane resin); the photocatalyst is anatase-form titanium oxide; and an electron uptake metal or antibacterial metal is added.

[0125]

In this case, the method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake ion or antibacterial metal ion, further adding thereto a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, putting the liquid into a mold for heat-curing and mold-release to obtain an intermediate member, and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0126]

Solutions including an electron uptake metal ion are: silver lactate, silver nitrate, silver sulfate, silver chlorate, silver fluoride, platinum sulfate, palladium rhodanide, palladium sulfate, aurous chloride, auric chloride, copper sulfate, cuprous acetate, cupric acetate, cupric sulfate, cupric chloride, cupric bromide, cupric nitrate, cupric chlorate, cupric rhodanide, ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, ferrous

iodide, ferrous bromide, ferricbromide, ferric oxalate, ferrous acetate, ferric acetate, ferrous chlorate, ferric chlorate, ferrous nitrate, ferric nitrate, ferrous thiosulfate, ferrous rhodanide, ferric rhodanide, cobalt chloride, cobalt sulfate, cobalt iodide, cobalt bromide, cobalt acetate, cobalt chlorate, cobalt nitrate, nickel chloride, nickel sulfate, nickel iodide, nickel bromide, nickel acetate, nickel chlorate, nickel nitrate, nickel rhodanide, zinc chloride, zinc sulfate, zinc iodide, zinc bromide, zinc acetate, zinc nitrate, and zinc chlorate. Such compound solutions of a soluble antibacterial metal are preferable, because a mixing treatment is easy.

[0127]

Solutions including an antibacterial metal ion are: silver lactate, silver nitrate, silver sulfate, cuprous sulfate, silver chlorate, silver fluoride, cuprous acetate, cupric acetate, cupric sulfate, cupric chloride, cupric bromide, cupric nitrate, cupric rhodanide, zinc chloride, zinc sulfate, zinc iodide, zinc bromide, zinc acetate, and zinc nitrate. Such compound solutions of a soluble antibacterial metal are preferable, because a mixing treatment is easy.

[0128]

Any solvent of a solution including an electron uptake metal ion or antibacterial metal ion, may basically be used, but water and alcohol are safe and easy to use. Also, use of the same kind of an anatase-form titanium oxide sol preferably makes a mixing treatment easy.

[0129]

In mixing an anatase-form titanium oxide sol with a

solution including an electron uptake metal ion or antibacterial metal ion, the pH of the solution including the antibacterial metal ion should be adjusted to be almost equal to the pH of the anatase-form titanium oxide sol; because a change in the pH of the anatase-form titanium oxide sol is small, without damaging remarkably the dispersion of the anatase-form titanium oxide sol in the suspension.

[0130]

After mixing the anatase-form titanium oxide sol with the solution including an electron uptake metal ion or antibacterial metal ion, a UV light may be irradiated on this solution. This allows the antibacterial metal to be photo-reducibly fixed on an anatase-form titanium oxide particle. Then, the electron uptake effect by the electron uptake metal after a photon is decomposed into a hole and an electron by a photocatalyst, can be delivered more effectively, and the electron to be recombined with the hole is lost by the same amount; therefore, a photocatalytic oxidative-decomposing action based on the hole is improved. Also, the released speed of the antibacterial metal ion can be controlled, providing an antibacterial action for a longer period.

[0131]

The most preferable usable examples are platinum, palladium and silver in the electron uptake metal; and silver in the antibacterial metal. Because, they do not change the speed of reaction wherein R part comprised of an alkyl group in a siloxane resin layer is oxidized (to be understood carboxylic oxidization) or decomposed

(Formula 1).

[0132]

For a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermoplastic resin; and the photocatalyst is anatase-form titanium oxide.

[0133]

In this case, the method is comprised of the steps of: applying anatase-form titanium oxide particles to an injection mold surface, injective-molding with a thermoplastic resin compound to obtain an intermediate member, and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a thermoplastic resin layer exposedly-formed on the surface of the intermediate member (Formula 1).

[0134]

For a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermoplastic resin; the photocatalyst is anatase-form titanium oxide; an electron uptake metal or antibacterial metal is added.

[0135]

In this case, the method is comprised of the steps of: applying a solution including an electron uptake metal ion or antibacterial metal ion to anatase-form titanium oxide particles for photo-reducibly fixing to make mixed particles, applying the mixed particles to an injection mold surface, injective-molding with a thermoplastic resin

compound to obtain an intermediate member, and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a thermoplastic resin layer exposedly-formed on the surface of the intermediate member (Formula 1).

[0136]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface shown in Fig. 4, one example is explained in the case where the substrate is quartz glass; and the hydrophilic photocatalyst is anatase-form titaniumoxide. In this case, the method is comprised of the steps of: applying to a quartz glass the precursor of anatase-form titanium oxide like titanium alkoxide; and calcining thereof.

[0137]

The precursor of anatase-form titanium oxide refers to a substance that is changed into anatase-form titanium oxide after calcining, including an organic titanic salt like titanium alkoxide and an inorganic titanic salt like titanium sulfate. Use of the precursor of these anatase-form titanium oxide allows preferably uniform application on a substrate. Also, after the precursor is changed into amorphous titanium oxide to cover the substrate uniformly, anatase-form titanium oxide crystal is formed, so that an interstice of 0.2  $\mu$ m or more is hard to be produced, and when the surface layer thickness is greater than a visible light wavelength, transparentness due to scattering is not lost. Therefore, a large amount of a means for maintaining an exposed surface hydrophilic is added to make prevention of rendering hydrophobic more

effectively.

[0138]

A method applying to quartz glass the precursor of anatase-form titanium oxide is explained below by taking an example in the case where titanium tetraethoxide ( $(C_2H_5O)_4Ti$ ), a kind of titanium alkoxide is used for the precursor of the anatase-form titanium oxide.

[0139]

First, a coating solution is made. The coating solution is made by adding a diluent and hydrochloric acid to titanium tetraethoxide. Alcohol such as ethanol and propanol is easy to handle for the diluent. However, water should not be included as much as possible. When a large amount of water is included, hydrolysis of metal alkoxide is promoted extraordinarily, causing a crack.

Hydrochloric is added to prevent an produced crack in after-drying and heat treatment.

[0140]

Next, the coating solution is applied on a substrate. A flow coating method to apply metal alkoxide is easier and preferable. The flow coating is preferably performed in the dry air. The dry air does not mean the air not including moisture at all, but the air with moisture less than that of the general air (atmosphere). When coating in the general air (atmosphere), hydrolysis is promoted too far due to moisture in the air, making film thickness control hard. Also, one retained amount of titanium tetraethoxide is  $100 \mu g/cm^2$  or less by conversion into that of titanium oxide; this is preferable in terms of prevention of a produced crack.

[0141]

After that, an amorphous titanium oxide film is formed by drying in the dry air for 1 - 10 minutes. Obtaining titanium oxide in the these steps is due to the principle shown below. First, titanium tetraethoxide, a start raw material reacts to a trace of moisture in the dry air mainly at flow coating for hydrolysis to generate titanium hydroxide. Further, dehydrating condensation reaction is produced at drying to generate amorphous titanium oxide on the substrate. A titanium oxide particle generated at this time is high purity of the order of some nm; for that reason, it is sintered at low temperatures compared with this titanium oxide.

[0142]

The application obtained from the above method is calcined at 400°C or more, amorphous titanium oxide is crystallized to obtain a stain-resistant member having an anatase-form titanium oxide film that is dense and has hydrophilicity.

[0143]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface shown in Fig. 4, one example is explained in the case where the substrate is soda glass; and the hydrophilic photocatalyst is anatase-form titanium oxide.

In this case, preferably, the method comprised of the steps of: applying to soda glass the precursor of silica glass like silicon alkoxide, applying thereon the precursor of anatase-form titanium oxide like titanium alkoxide, and calcining thereof.



[0144]

Preferably, a high purity silica layer is interleaved between a substrate and a surface layer, so that an alkaline component in soda glass is dispersed on the surface, to adhere to the active point of anatase-form titanium oxide, preventing effectively a photocatalytic activation from being lowering.

Such effect is efficient like soda glass, when an alkali metal such as sodium and potassium, and an alkaline earth metal such as magnesium and calcium are included in the substrate.

[0145]

Applying to soda glass the precursor of silica glass like silicon alkoxide is performed below. First, a coating solution is made.

The coating solution is made by adding a diluent, water and hydrochloric acid to silicon alkoxide like tetraethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ).

The water is added to promote hydrolysis, because silicon alkoxide is stable compared with alkoxide, a transition metal such as titanium, and is resistant to hydrolysis.

The coating solution made is heated by adding water; therefore, it should be left for about one hour, before flow coating onto the substrate.

[0146]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is a tile; the hydrophilic photocatalyst is anatase-form titanium

oxide; further tin oxide is added as a particle that fills an exposed surface. In this case, the method is comprised of the steps of: applying to a substrate surface an anatase-form titanium oxide sol, calcining thereof, applying a tin oxide sol to the surface, and drying thereof.

[0147]

Sintering is preferably performed so that lowering of photocatalytic activation due to a lowered specific surface area with particle growth is less; the treatment is made at low temperatures to a degree that a large interstice is hard to be generated with a secondary particle growth, and at high temperatures to a degree that the interstice rate of the surface layer is as low as possible. For example, when using a sol with an average particle diameter of  $0.01 \mu\text{m}$  for a start raw material, the treatment is preferably made at about  $400 - 900^{\circ}\text{C}$ .

[0148]

In applying a tin oxide sol to the surface, it is preferable to select a tin oxide sol with the average diameter shorter than that of the interstice on the surface layer. To select it, when a titanium oxide sol with an average particle diameter of  $0.01 \mu\text{m}$  is used for the above start raw material and calcined at about  $400 - 900^{\circ}\text{C}$ , a tin oxide sol with an average diameter shorter than the particle diameter of titanium oxide at a calcining temperature, is used. The particle diameters are less than  $0.01 - 0.02 \mu\text{m}$  at  $700^{\circ}\text{C}$  or less, less than  $0.04 \mu\text{m}$  at  $750^{\circ}\text{C}$ , less than  $0.1 \mu\text{m}$  at  $850^{\circ}\text{C}$ , and less than  $0.3 \mu\text{m}$  at  $900^{\circ}\text{C}$ . It is preferable to use a tin oxide sol with an average particle diameter as short as possible in the above range.

[0149]

Drying may be treated at temperatures to a degree that free water is vaporized, i.e. at 100°C or more.

[0150]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is a tile; the hydrophilic photocatalyst is anatase-form titanium oxide; further tin oxide is added as a sintering assistant.

In this case, the method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a tin oxide sol, applying the mixture on a substrate surface, and calcining thereof.

When, for example, a titanium oxide sol with an average particle diameter of 0.01  $\mu$ m is used for a start raw material, calcining is made at 750°C or more, making the member dense with preferable wear resistance.

[0151]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is quartz glass; the hydrophilic photocatalyst is anatase-form titanium oxide; further an electron uptake metal or antibacterial metal is added.

In this case, the method is comprised of the steps of: applying to a substrate surface the precursor of anatase-form titanium oxide like titanium alkoxide, calcining thereof, applying to the surface a solution including an electron uptake metal ion or antibacterial metal ion, and irradiating a UV light.

[0152]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is soda glass; the hydrophilic photocatalyst is anatase-form titanium oxide; further an electron uptake metal or antibacterial metal is added. In this case, preferably the method is comprised of the steps of: applying to soda glass the precursor of silica glass like silicon alkoxide, applying thereon the precursor of anatase-form titanium oxide like titanium alkoxide, calcining thereof, applying to the surface a solution including an electron uptake metal ion or antibacterial metal ion, and irradiating a UV light.

[0153]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 5, one example is explained in the case where the substrate is aluminum; the hydrophilic photocatalyst is anatase-form titanium oxide; and the hydrophilic substance is a substance wherein a thermosetting resin (siloxane resin) is rendered hydrophilic.

One method in this case is comprised of the steps of: adding a siloxane resin to an anatase-form titanium oxide sol to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on

the surface of the intermediate member by UV light irradiation (Formula 1).

[0154]

Any method of applying a liquid to a substrate surface may basically be used, but a spray coating and roll coating methods are relatively easy.

[0155]

The other method is comprised of the steps of: applying to an aluminum substrate surface a mixture of a siloxane resin with a curing agent to form a base coat layer, adding thereon the siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid to be applied to the substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0156]

The Auger electron spectroscopy results of the element analysis in the cross-sectional direction of the above intermediate member, are shown in Fig. 7 (a) - (c). Nitric acid was used for dispersion of an anatase-form titanium oxide sol, and a heat-curing treatment was made at 150°C. In Fig. 7 (a), Si, C, N and O can be observed on a sample outermost surface; but Ti not. However, as shown in Fig. 7 (b), Ti as well as Si, C, N and O can be observed at 200 nm under the sample outermost surface. At 200 nm under the surface is a layer comprised only of a siloxane resin, and only Si, C and O that are components thereof can be observed

(Fig. 7 (c)). Thus, it is understood that one layer comprised only of a siloxane resin layer is formed on the sample outermost surface of the intermediate member made by the above making method in this way.

R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of this intermediate member by UV light irradiation, is decomposed or oxidized to be rendered hydrophilic by the action of active oxygen generated from anatase-form titanium oxide at about 20 nm under the surface.

[0157]

The UV light refers to a light including a light with a short wavelength to a degree of energy enough to excite an electron from a valence electron band to a conductive band in a substance having a photocatalytic function, so that a light including a light of less than 400 nm is irradiated for anatase-form titanium oxide.

[0158]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 5, one example is explained in the case where the substrate is a resin; the hydrophilic photocatalyst is anatase-form titanium oxide; and the hydrophilic substance is a substance wherein a thermosetting resin (siloxane resin) is rendered hydrophilic.

One method in this case is comprised of the steps of: adding a siloxane resin to an anatase-form titanium oxide sol to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the

diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0159]

The other method is comprised of the steps of: applying to a substrate surface a mixture of a siloxane resin with a curing agent to form a basecoat layer, adding thereon the siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid to be applied to the substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0160]

Heat-curing may be performed at low temperatures of less than 100°C for a long time, or at 100°C or more and at less than the heat-resistant temperatures of the substrate and base coat layer for a short time. In general, on a surface layer, a photocatalyst has a specific gravity greater than that of a resin. Heat-curing at 100°C or more and at less than the heat-resistant temperatures of the substrate and base coat layer is preferable, because a photocatalyst is concentrated on the upper part, so as to shorten the time for decomposing or oxidizing to be rendered hydrophilic R part comprised of an alkyl group in a siloxane

resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation.

[0161]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 5, one example is explained in the case where the substrate is a resin; the hydrophilic photocatalyst is anatase-form titanium oxide; the hydrophilic substance is a substance wherein a thermosetting resin (siloxane resin) is rendered hydrophilic; further an electron uptake metal or antibacterial metal is added.

One method in this case is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an antibacterial metal ion, adding thereto a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0162]

Another method is comprised of the steps of: adding to an anatase-form titanium oxide sol a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof, applying to the surface a solution



including an antibacterial metal ion, irradiating thereon a UV light to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0163]

Still another method is comprised of the steps of: adding to an anatase-form titanium oxide sol a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1), applying to the surface a solution including an antibacterial metal ion, and irradiating thereon a UV light.

In these 3 methods, a base coat layer may be interleaved.

[0164]

The advantage of the construction in Fig. 5 is that a surface layer can be formed at low temperatures of about 100°C. Therefore, a surface layer can later be formed on ready-made glass, plastic, metal and ceramic with the above method. Also, the same effect can be expected, even when a film in Fig. 3 or an application comprised of a photocatalyst and a photo-resistant resin is stuck on ready-made glass, plastic, metal and ceramic.

[0165]

For a member wherein a surface layer comprised of a photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 6 and an exposed surface is comprised only of a hydrophilic substance, one example is explained in the case where the substrate is aluminum; the hydrophilic substance is glass; and the photocatalyst is anatase-form titanium oxide.

The advantage of the construction in Fig. 6 is that the surface can be made of glass harder than a resin, and an exposed surface is dense even if powder-like matter is used for a start raw material of the photocatalyst. However, when the particle diameter of the powder is too large, it lowers maintaining and recovering effects of a hydrophilic surface by the photocatalyst; thus, the diameter is preferably 0.3  $\mu$ m or less.

[0166]

One method in this case is comprised of the steps of: applying to a substrate an anatase-form titanium oxide sol, calcining thereof, and applying thereto glass frit for recalcining.

[0167]

The other method is comprised of the steps of: applying to a substrate an anatase-form titanium oxide sol, and applying thereto glass frit for calcining.

[0168]

For a member wherein a surface layer comprised of a photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 6 and an exposed surface is comprised only of a hydrophilic substance, one example is

explained in the case where the substrate is aluminum; the hydrophilic substance is glass; the photocatalyst is anatase-form titanium oxide; and an electron uptake metal or antibacterial metal is added.

One method in this case is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake metal ion or antibacterial metal ion, applying the mixture to a substrate, calcining thereof, and applying thereto glass frit for recalcining.

[0169]

Another method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake metal ion or antibacterial metal ion, applying the mixture to a glass substrate, and applying thereto glass frit for calcining.

[0170]

Still another method is comprised of the steps of: applying to a substrate an anatase-form titanium oxide sol, calcining thereof, applying thereto glass frit for recalcining to apply to the surface a solution including a metal ion, and irradiating thereon a UV light.

[0171]

Further method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake metal ion or antibacterial metal ion, applying the mixture to a glass substrate, applying thereto glass frit for calcining to apply to the surface a solution including a metal ion, and irradiating thereon a UV light.

[0172]

The light irradiating means can indoor illumination and

sunray, but a light with high UV intensity should be irradiated on a member surface to improve maintaining and recovering effects of hydrophilicity.

For this reason, for example, a means for irradiating a UV light should be provided on the whole rim of the member or part thereof.

Also, in this case, providing a skirt-like reflecting means so that a means for irradiating a UV light is enclosed, can preferably improve the intensity of a UV irradiated on a mirror surface.

[0173]

In another method, a multiple of transparent plates may be stuck together to make a member, and a means for irradiating a UV light may be interleaved between the members. In this case, the means for irradiating a UV light is preferably a flat light source. Such construction can improve the intensity of a UV irradiated on a mirror surface. In such case, a light source is preferably turned OFF during use, but it is safe if turned ON by mistake, because a UV is absorbed by the photocatalyst on a surface layer.

[0174]

The effect of hydrophilicity maintenance of the above member is explained below based on the experiment examples. (Example 1)

Tetraethoxysilane, 36% hydrochloric acid, pure water and ethanol, are mixed at a ratio by weight of 6 : 2 : 6 : 86, and the mixture was left for one hour. Then, the mixture was applied to soda glass by the flow coating method to obtain an intermediate member P. Further, titanium

tetraethoxide and ethanol were mixed at a ratio by weight of 1 : 9. The 36% hydrochloric acid of 10% by weight versus titanium tetraethoxide, was added to the mixture to make a coating liquid. This coating liquid was applied to the surface of the intermediate member P in the dry air by the flow coating method. The amount of one application was  $45 \mu\text{g}/\text{cm}^2$  by converting into titanium oxide.

After that, the liquid was dried in the dry air for 1 - 10 minutes, further calcined at  $500^\circ\text{C}$  to obtain an embodiment sample A.

A 1% silver lactate water solution by weight was applied to the surface of the embodiment sample A, and was subjected to a BLB fluorescent lamp of 20 W at a distance of 20 cm for one minute to obtain an embodiment sample B. Still, the water-absorbed rate of both of the embodiment samples A and B was less than 1%.

[0175]

The contact angle with water and wear resistance in the embodiment samples A and B, for the purposes of comparison, soda glass and the intermediate member P, were evaluated.

The contact angles with water of the samples after making and the samples subjected to a BLB fluorescent lamp for one month, were evaluated with a contact angle measuring instrument.

In the wear-resistant test, slided wearing with a plastic eraser was performed, and changes in an appearance were compared for evaluation. The evaluating references are shown below.

◎: No change in 40 reciprocated slidings.

○: 10 or more and less than 40 slidings caused a surface

layer to be scratched and peeled off.

Δ: 5 or more and less than 10 slidings caused a surface layer to be scratched and peeled off.

×: Less than 5 slidings caused a surface layer to be scratched and peeled off.

[0176]

[Table 1]

[0177]

Because the soda glass substrate is considerably rendered hydrophobic in terms of a contact angle with water of 50°, water droplets were observed apparently. On the contrary, the embodiment samples A and B, and the intermediate member P had a low contact angle with water of about less than 1°, and the surfaces were sufficiently rendered hydrophilic, observing no water droplets.

After being subjected to the BLB fluorescent lamp for one month, the contact angle with water was 53° of the glass substrate, and 49° of the intermediate member P, and the surfaces were considerably rendered hydrophobic, observing water droplets apparently. In contrast with this, the contact angle with water of both of the embodiment samples A and B was low with about less than 1°, showing the maintained hydrophilicity. No water droplets were observed.

[0178]

Next, the recovering effects of hydrophilicity in the embodiment samples A and B, and C made as shown below, were checked.

The embodiment sample C was made in the following manner. After soda-lime glass was washed with 0.1 M

hydrochloric acid in hot water, titanium tetraethoxide and ethanol were mixed at a ratio by weight of 1 : 9. The 36 % hydrochloric acid of 10 % by weight versus titanium tetraethoxide, was added to the mixture to make a coating liquid. This coating liquid was applied to the surface of the soda-lime glass in the dry air by the flow coating method. The amount of one application was  $45 \mu\text{g}/\text{cm}^2$  by converting into titanium oxide. After that, the liquid was dried in the dry air for 1 - 10 minutes, further calcined at  $500^\circ\text{C}$  to obtain a sample.

In the recovering effects of hydrophilicity, the sample surfaces were wiped off with alcohol to improve the contact angle with water on the surface, then subjected to a BLB with  $0.5 \text{ mW}/\text{cm}^2$  UV output to measure a time-varying change in the contact angle with water.

[0179]

The results are shown in Fig. 8. The contact angles of the samples A - C were all reduced as time elapsed. However, compared with the sample C, the contact angles of the samples A and B were reduced at a dramatic rate, becoming already  $0^\circ$  30 minutes later.

[0180]

Then, the antibacterial properties of the embodiment sample B and a soda glass substrate, were checked.

They were evaluated with a colon bacillus (*Escherichia coli* W3110 stock).

Glass plates (100 X 100) on which an bacterial liquid of 0.15 ml (10000 - 50000CFU) was dropped, were contacted on the outermost surfaces of the above samples sterilized with 70% ethanol beforehand and, and then were subjected to

irradiation of a white light (3500 lux) for 30 minutes. The bacterial liquid thereon was wiped away with sterilized gauze to be recovered to a physiological salt water of 10 ml. Then, the survival rate of the bacteria was found for an evaluating index. The evaluating indexes are shown below.

- ◎: The survival rate of the colon bacillus is less than 10%.
- : The survival rate of the colon bacillus is 10% or more and less than 30%.
- △: The survival rate of the colon bacillus is 30% or more and less than 70%.
- ×: The survival rate of the colon bacillus is 70% or more.

As a result, the soda glass substrate showed ×; while the embodiment sample B showed a favorable result of ◎.

[0181]

(Example 2)

A mixture wherein a curing agent was added to a siloxane resin was applied to a transparent acrylic, plastic substrate of 10 cm square and was heat-treated at 150°C to obtain an intermediate member S.

Each of siloxane resins of 5%, 10%, 50% and 80% by weight versus the sum of the titanium oxide solid content and siloxane resin, was added to a nitric acid peptization type suspension of a titanium oxide sol with an average particle diameter of 0.01  $\mu$ m, was diluted with propanol, and was subjected to a curing agent to obtain a liquid. This liquid was applied to the surface of this intermediate member S for heat-treatment at 150°C to obtain an



intermediate member T.

This intermediate member T was subjected to a BLB lamp of  $0.5 \text{ mW/cm}^2$  for desired time to obtain an embodiment sample. Still, the water-absorbed rate of the sample was less than 1 %.

In the embodiment sample and the intermediate member S, the relation between lamp irradiated time and hydrophilic degree, hydrophilicity and maintenance thereof, recovering effect, wear resistance, and surface hardness, were evaluated.

The surface hardness was evaluated with a hardness wherein a member surface was scratched with a pencil with different hardnesses of 6B - 9H to produce scoring.

[0182]

Fig. 9 shows the relation between lamp irradiated time and hydrophilic degree, when the ratio by weight of the titanium oxide solid content versus the titanium oxide solid content and siloxane resin in the surface layer was changed. The contact angle with water of the intermediate member S was not changed, but the contact angles with water of all samples to which 20%, 50%, 90% and 95% by weight were added, were lowered to about  $3^\circ$  by irradiation within 200 hours. Also, the angle of the sample to which 5 % by weight was added, was lowered to about  $10^\circ$  by lamp irradiation for 200 hours. Thus, it was apparent that all the samples show the preferable hydrophilicity.

[0183]

The evaluating results of the wear resistance are shown in Fig. 10. For the purposes of comparison, the sample wherein a surface layer was formed without adding a siloxane

resin was also evaluated. As a result, the ratio by weight of the titanium oxide solid content versus the sum of the titanium oxide solid content and siloxane resin in the surface layer was 95% or less by weight, showing ○; and was 90% or less by weight showing ◎, with favorable results obtained.

[0184]

The evaluated results of the surface hardness are shown in Fig. 11. The ratio by weight of the titanium oxide solid content versus the sum of the titanium oxide solid content and siloxane resin in the surface layer was 90%, showing about 5B, and was 60%, showing H. Thus, the tendency that the hardness was increased with an increase in the siloxane resin, was observed.

[0185]

Using the same method as Example 1, to evaluate the hydrophilicity and maintaining and recovering effects thereof, the ratio by weight of the titanium oxide solid content versus the sum of the titanium oxide solid content and siloxane resin in the surface layer was 50%, and samples subjected to a lamp for 10 hours, were used. As a result, the contact angles with water of the sample immediately after irradiation, and the sample subjected to irradiation for one month, were less than 3° which showed preferable hydrophilicity; it proved that the effect is maintained.

The sample surfaces were wiped off with alcohol to improve the contact angle with water on the surface, then subjected to a BLB with 0.5 mW/cm<sup>2</sup>UV output to measure a time-varying change in the contact angle with water;

irradiation for about one hour lowered the angle from 30° to about 1°.

[0186]

(Example 3)

A mixture wherein a curing agent was added to a siloxane resin was applied to a 10-cm square tile substrate and was heat-treated at 150°C to obtain an intermediate member K.

A siloxane resin of 50 % by weight versus the sum of the titanium oxide solid content and siloxane resin, was added to a solution wherein a nitric acid peptization type suspension of a titanium oxide sol with an average particle diameter of 0.01  $\mu$ m, was mixed with a copper acetate solution with pH that was made almost equal to the pH of the titanium oxide sol by nitric acid, was diluted with propanol, and was subjected to a curing agent to obtain a liquid. This liquid was applied to the surface of this intermediate member S for heat-treatment at 150°C to obtain an external wall embodiment member. Still, the ratio by weight of copper versus the titanium oxide in the embodiment member was 2%. The water-absorbed rate of the sample was less than 1%. The obtained sample and the intermediate member K for comparison, were exposed outdoor for a long period, to evaluate a change in a contact angle with water and stain adhesion.

[0187]

The results are shown in Fig. 12. According to the diagram, the contact angle with water was about 3° 2 days later, showing no change even after 6000-hour exposure.

Also, a large amount of stains adhered to the

intermediate member K, but almost no stain on the embodiment sample was observed.

[0188]

(Example 4)

Enamel and a titanium oxide sol were applied to a tile substrate to be calcined at 880 A, rendered thereof to a copper acetate solution, dried thereof, and subjected thereof a BLB lamp to obtain an embodiment sample. The obtained sample and a glazed tile for comparison, were exposed outdoor for a long period, to evaluate a change in a contact angle with water and stain adhesion. As a result, 60 days later, a large amount of stains adhered to the glazed tile, but almost no stain on the embodiment sample was observed.

[0189]

[Effect of the Invention]

A member is provided with an exposed surface hydrophilic and a means for maintaining thereof like a photocatalyst, so as to be resistant to organic stains like oil for a long period.

[Brief Description of the Drawings]

Fig. 1

It is a diagram showing the relation between a contact angle with water and stain adhesion.

Fig. 2

It is a diagram showing an evaluating apparatus for stain resistance.

Fig. 3

It is a diagram showing one embodiment of the present

invention.

Fig. 4

It is a diagram showing another embodiment of the present invention.

Fig. 5

It is a diagram showing another embodiment of the present invention.

Fig. 6

It is a diagram showing another embodiment of the present invention.

Fig. 7

It is an Auger electron spectroscopy profile diagram of an intermediate member produced in the producing step of an antifogging transparent member according to the present invention; (a) is a sample outermost surface, (b) is at 20 nm under the sample outermost surface, and (c) is at 200 nm under the sample outermost surface.

Fig. 8

It is a diagram showing the recovering effect of hydrophilicity of the embodiment according to the present invention.

Fig. 9

It is a diagram showing the relation between lamp irradiated time and hydrophilic degree of the embodiment according to the present invention.

Fig. 10

It is a diagram showing the relation between the weight of titanium oxide and wear resistance in the surface layer of the embodiment according to the present invention.

Fig. 11

It is a diagram showing the relation between the weight of titanium oxide and surface hardness in the surface layer of the embodiment according to the present invention.

Fig. 12

It is a diagram showing the result in an outdoor exposure test of the embodiment according to the present invention.

[Explanation of the Reference Numerals]

- 1 ... Sample,
- 2 ... Artificial bathtub water,
- 3 ... Dirt,
- 4 ... Level surface,
- 5 ... Film comprised of a hydrophilic substance,
- 6 ... Photocatalyst,
- 7 ... Substrate,
- 8 ... Layer comprised of a hydrophilic photocatalyst,
- 9 ... Hydrophilic substance non-photocatalytic,
- 10 ... Hydrophilic photocatalyst,
- 11 ... Exposed surface formed by a hydrophilic substance non-photocatalytic

Formula 1

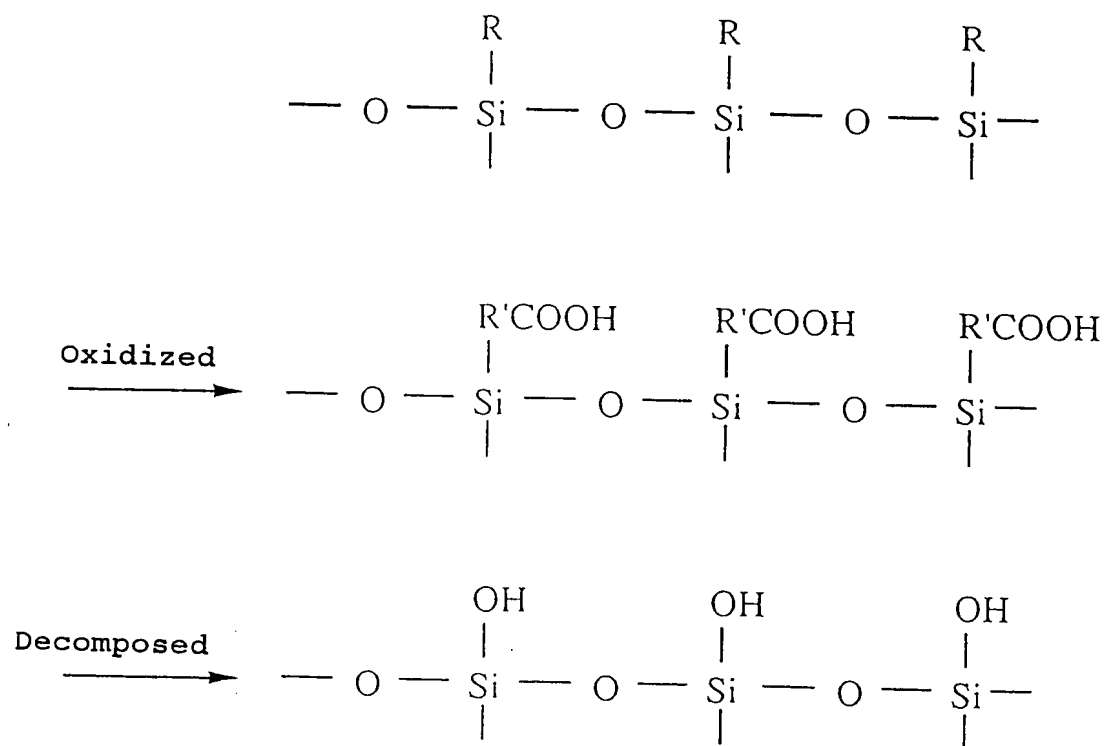


Table 1

Sample	After making sample		One month later	
	Contact angle with water (°)	Wear resistance	Contact angle with water (°)	Wear resistance
Embodiment sample A	< 1	◎	< 1	◎
Embodiment sample B	< 1	◎	< 1	◎
Soda glass	50	◎	53	◎
Intermediate member P	< 1	◎	49	◎

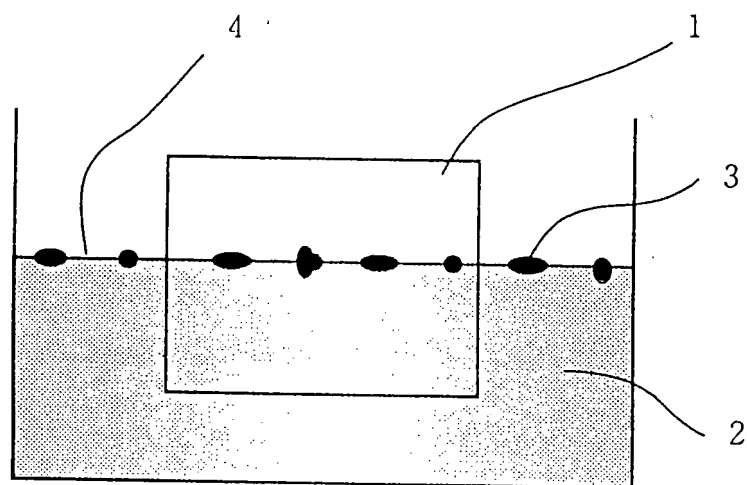


Fig. 1

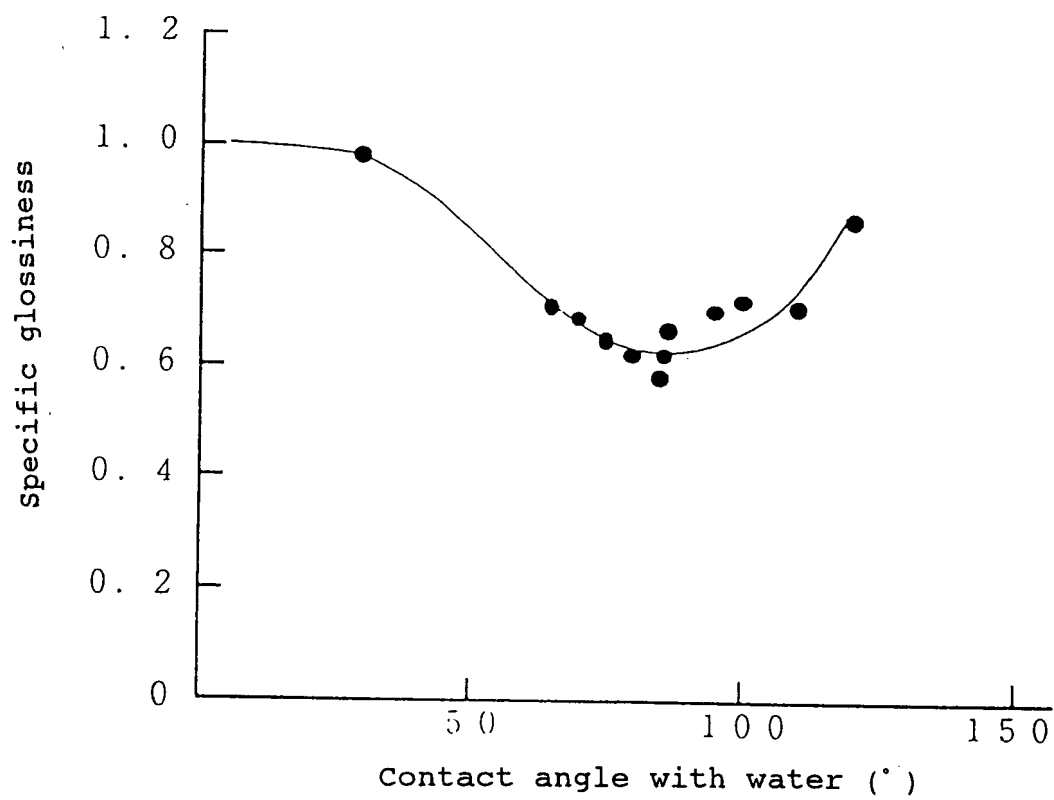


Fig. 2



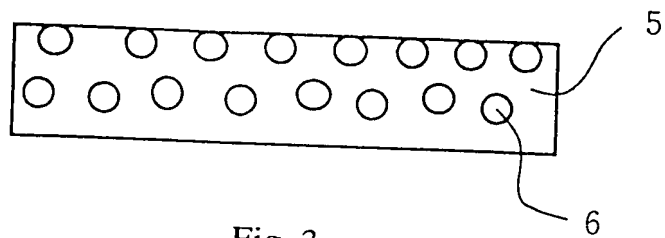


Fig. 3

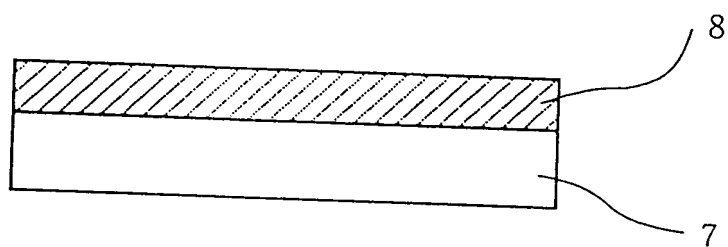


Fig. 4

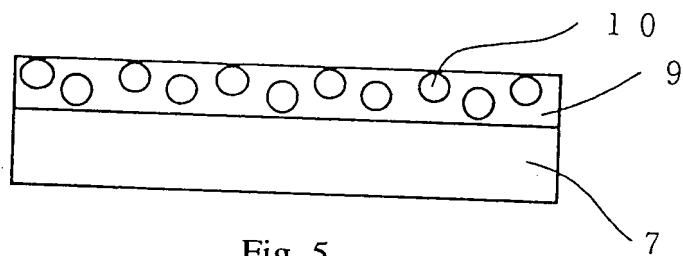


Fig. 5

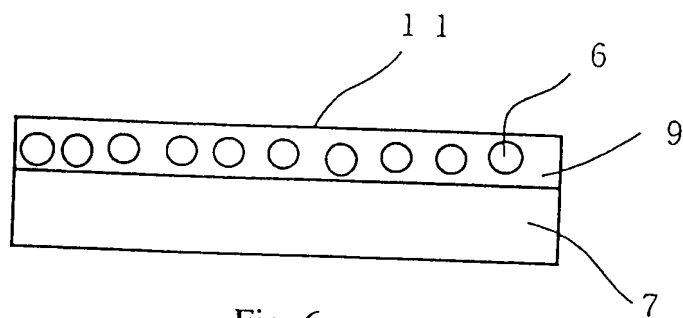


Fig. 6

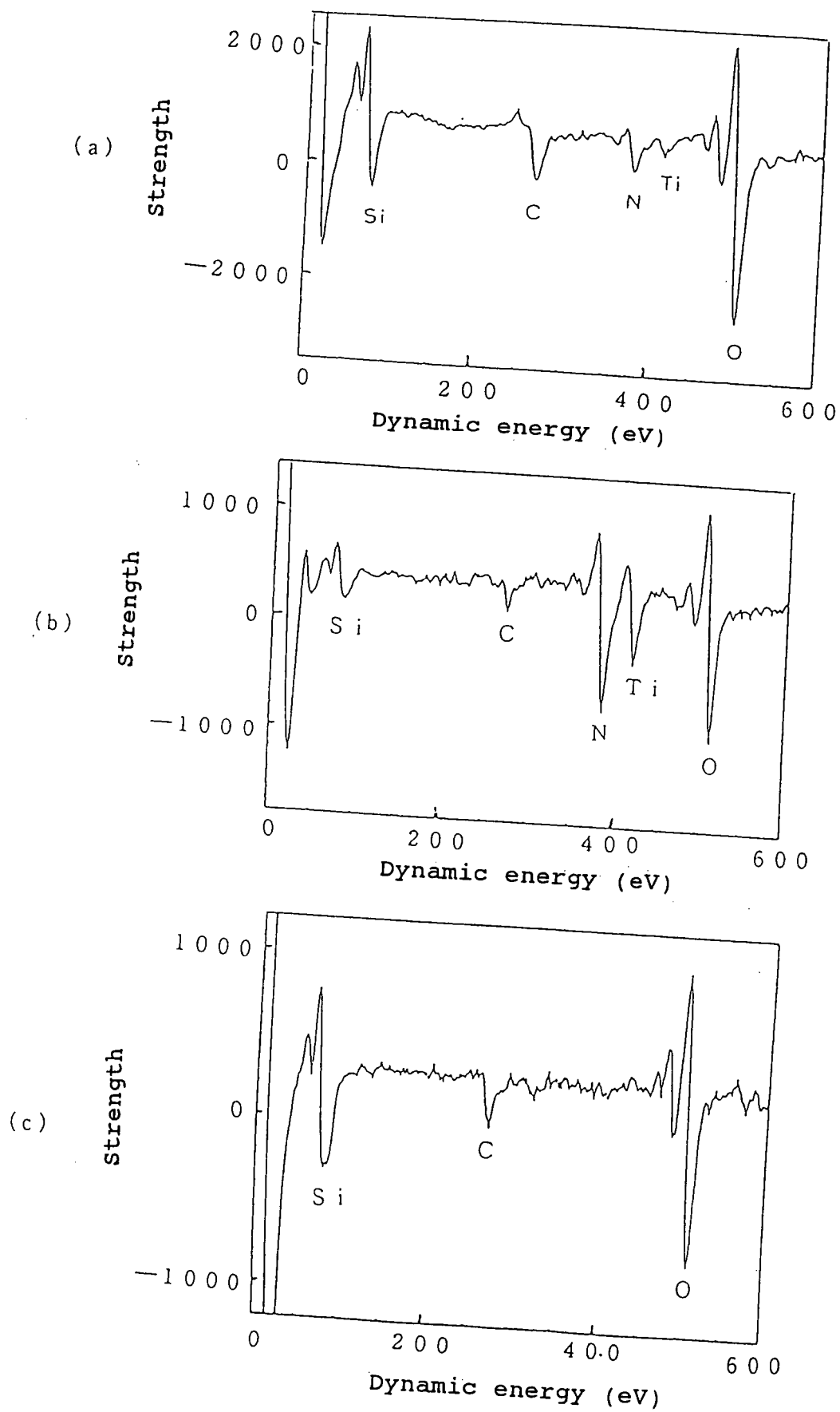


Fig. 7

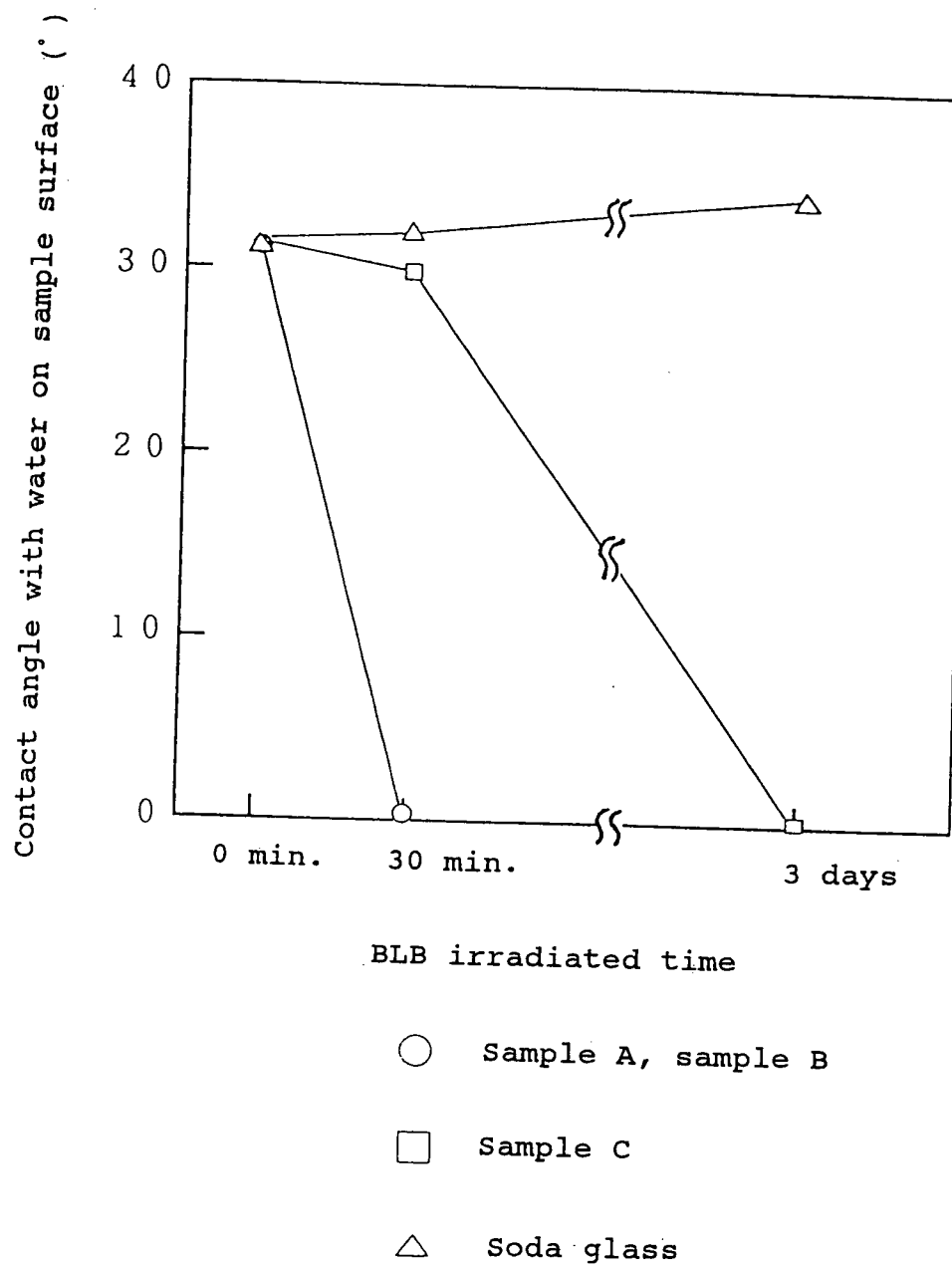
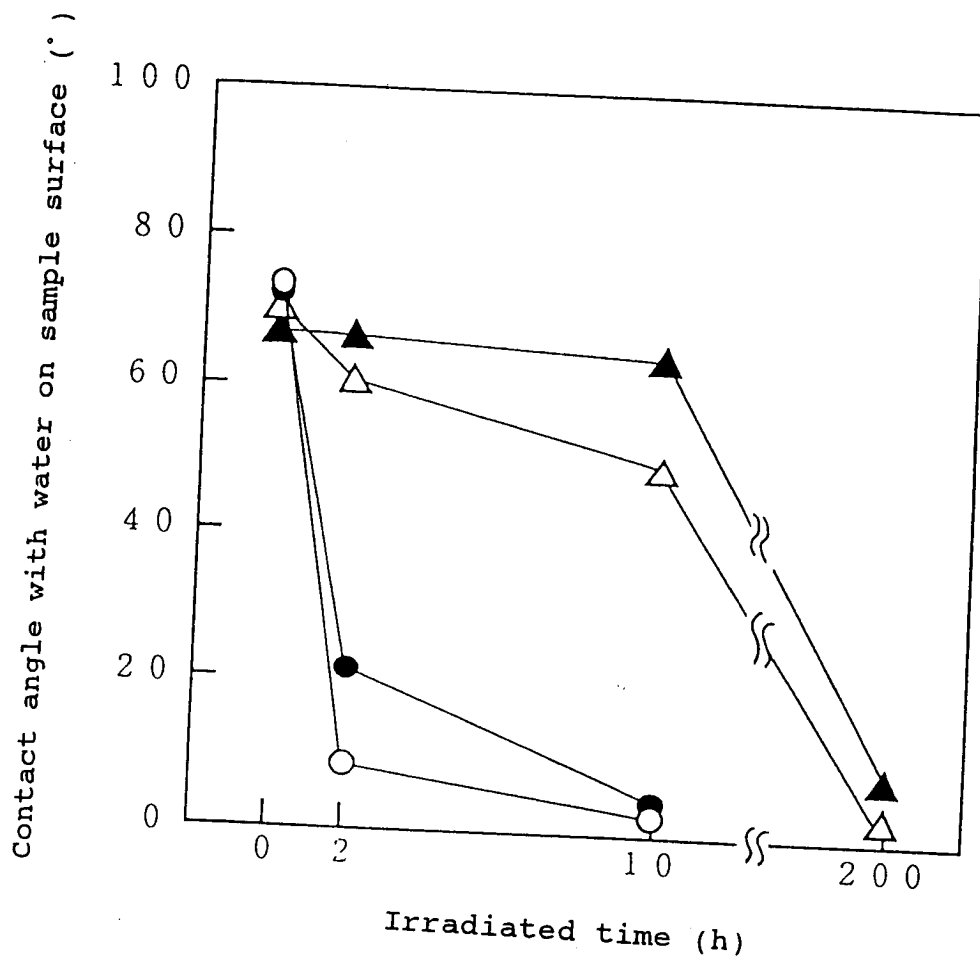


Fig. 8



- ▲ TiO<sub>2</sub> 5%
- △ TiO<sub>2</sub> 10%
- TiO<sub>2</sub> 50%
- TiO<sub>2</sub> 80%

Fig. 9

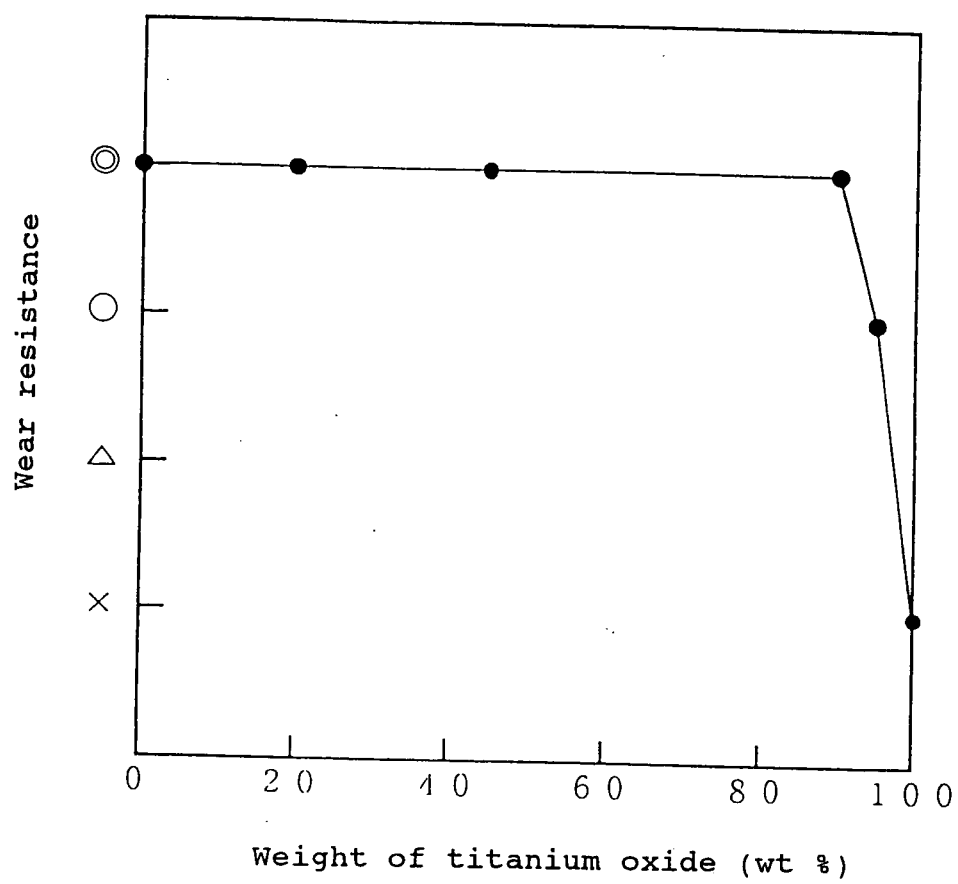


Fig. 10

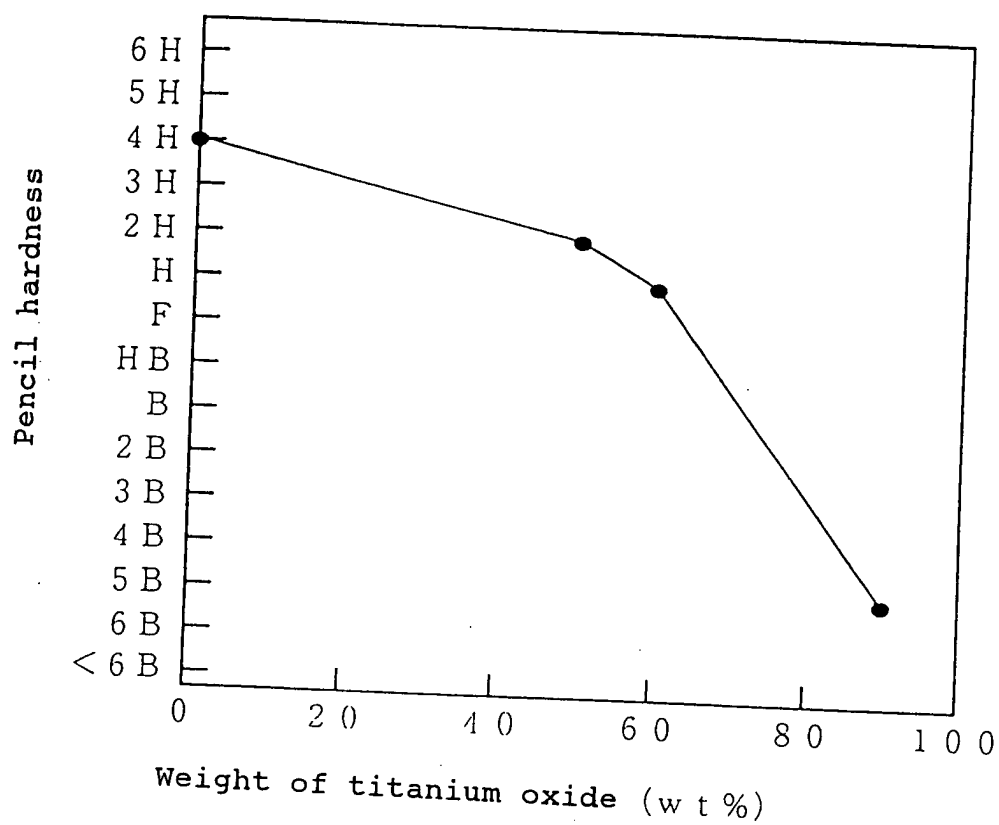
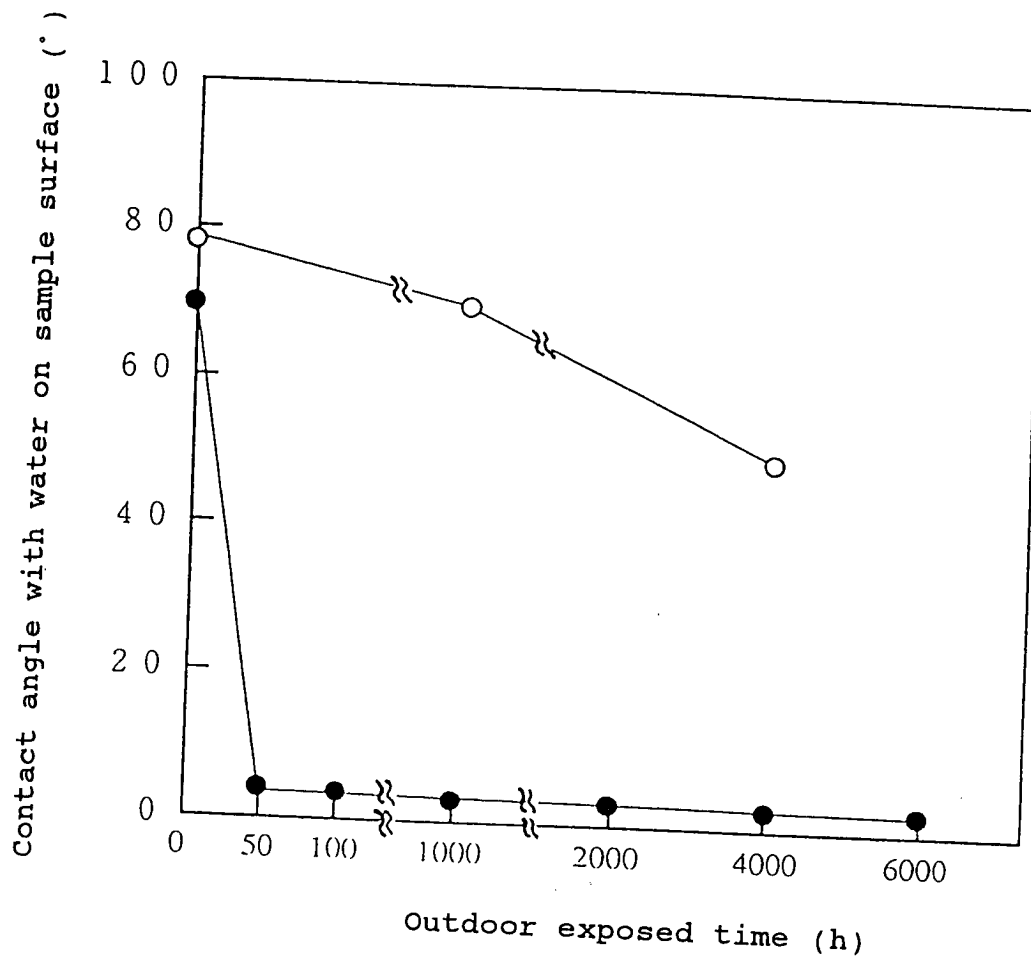


Fig. 11



○ Intermediate member  
● Embodiment sample

Fig. 12

# ABSTRACT

## [Objects]

It is an object to provide a member that is resistant to organic stains like oil for a long period.

## [Constitution]

A stain-resistant member having an exposed surface hydrophilic (5) and a means for maintaining thereof (6).

## [Selected Drawing]

Fig. 5